

# A hybrid variational-perturbation calculation of the ro-vibrational spectrum of nitric acid

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## Abstract

Rotation-vibration spectra of the nitric acid molecule,  $\text{HNO}_3$ , are calculated for wavenumbers up to  $7000\text{ cm}^{-1}$ . Calculations are performed using a Hamiltonian expressed in internal curvilinear vibrational coordinates solved using a hybrid variational-perturbation method. An initial potential energy surface (PES) and dipole moment function (DMF) are calculated *ab initio* at the CCSD(T)/aug-cc-pVQZ level of theory. Parameters of the PES and DMF are varied to minimize differences between the calculated and experimental transition frequencies and intensities. The average, absolute deviation between calculated and experimental values is  $0.2\text{ cm}^{-1}$  for frequencies in the fundamental bands and  $0.4\text{ cm}^{-1}$  for those in the first overtone and lowest combination bands. For the intensities, the calculated and experimental values differ by 0.3% and 40% for the fundamentals and overtones, respectively. The optimized PES and DMF are used to calculate the room-temperature ro-vibrational spectrum. These calculation reproduce both the form of the absorption bands, and fine details of the observed spectra, including the rotational structure of the vibrational bands and the numerous hot absorption band. Many of these hot bands are found to be missing from the compilation in HITRAN. A room temperature line list comprising  $2 \times 10^9$  lines is computed.

## I. INTRODUCTION

Nitric acid ( $\text{HNO}_3$ ), in spite of its low concentration, makes a significant contribution to the infrared (IR) spectrum of the Earth's atmosphere, since it has a number of strong absorption bands lying in the water transparency window [1–6]. Yet its spectrum remains poorly characterized with, for example, no transition wavenumbers above  $2000\text{ cm}^{-1}$  included in the HITRAN database [7], despite the fact that several fundamental bands lie at higher wavenumbers. This issue is not due to any lack of attempts to measure the IR spectrum of  $\text{HNO}_3$  [8–51], but rather to do with the difficulty of interpreting its spectrum and making line assignments. Experimental line intensities have also been the subject of number of studies [19, 39, 44, 46, 52–56].

The study of the  $\text{HNO}_3$  spectrum over a range of temperatures is a difficult experimental and theoretical problem. Experimental study of the  $\text{HNO}_3$  IR spectrum is challenging because in the gas phase it is a mixture containing significant numbers of dimers and complexes, as well as the products of its dissociation ( $\text{NO}_2$ ,  $\text{H}_2\text{O}$ ,  $\text{O}_2$ ). Therefore, experimental  $\text{HNO}_3$  spectra are usually processed spectra in which spectra due to dimers, complexes and dissociation products have been subtracted. In addition,  $\text{HNO}_3$  is a chemically aggressive species, which greatly complicates the experimental study of its spectrum at higher temperatures.

From the theoretical perspective, study of the ro-vibrational infrared spectrum of the  $\text{HNO}_3$  is difficult because of the relatively large number of the vibrational degrees of freedom,  $N_c = 9$ , and the large anharmonicity of its vibrations. There are only limited attempts to solve the vibrational and ro-vibrational problems using full-dimensionality [47, 57–60]. Benderskii and Vetoshkin [57] used a perturbative approach to study the tunneling dynamics of internal rotation. Lauvergnat and Nauts [58] also concentrated on these levels in both reduced and full dimensionality. Konen *et al* [47] used second-order vibrational perturbation theory (VPT2) to help interpret their experimental findings. More recently, Avila and Carrington [59, 60] have performed full-dimensional variational calculations with a particular focus on how to make such studies efficient. None of these studies considered transition intensities and amongst various *ab initio* studies using more approximate treatments [61–66], only Lee and Rice [61] appear to have considered (harmonic) intensities.

Recently, we [67] developed a hybrid variational-perturbational calculation scheme for computing IR spectra of polyatomic species.  $\text{HNO}_3$  was one of the species used to test this methodology. Here we present calculations of the infrared spectrum of  $\text{HNO}_3$  performed using this method. The calculations provide a comprehensive room temperature line list covering the range  $0 - 7000\text{ cm}^{-1}$ .

## II. HAMILTONIAN

Our vibration-rotation Hamiltonian written in curvilinear internal coordinates and an Eckart embedding has the form [68]

$$\hat{H}_{vr} = \hat{H}_v - \frac{\hbar^2}{2} \sum_{a,b} \frac{\partial}{\partial \xi_a} \mu_{ab}(\underline{q}) \frac{\partial}{\partial \xi_b}, \quad \xi_a, \xi_b = \alpha, \beta, \gamma, \quad (1)$$

where  $\underline{\xi}$  are the rotational coordinates and  $\hat{H}_v$  is the vibrational part of the Hamiltonian

$$\hat{H}_v = \hat{T}_v + V(\underline{q}) \quad (2)$$

$$\hat{T}_v = -\frac{\hbar^2}{2} \sum_{i,j} t^{\frac{1}{4}} \frac{\partial}{\partial q_i} g_{ij}(\underline{q}) t^{-\frac{1}{2}} \frac{\partial}{\partial q_j} t^{\frac{1}{4}}. \quad (3)$$

Here  $q_i$  are internal, vibrational curvilinear coordinates given by changes in the bond lengths, valence bond angles, and dihedral angles from the corresponding equilibrium values;  $\alpha, \beta, \gamma$  are the Euler angles between the axes of the equilibrium moment of inertia tensor and external Cartesian coordinate axes;  $\mu_{ab}(\underline{q})$  are elements of the inverse of the moment of inertia tensor,  $\underline{I}(\underline{q})$ ;  $\hat{T}_v$  is the vibrational kinetic energy operator and  $g_{ij}(\underline{q})$  are elements of the kinetic energy coefficients matrix  $\underline{G}(\underline{q})$  and  $t = \det[\underline{G}]$ . Finally,  $V(\underline{q})$  is the molecular potential energy.

After transformation, the vibrational kinetic operator can be written as

$$\hat{T}_v = -\frac{\hbar^2}{2} \sum_{i,j} \frac{\partial}{\partial q_i} g_{ij}(\underline{q}) \frac{\partial}{\partial q_j} + \beta(\underline{q}), \quad (4)$$

where

$$\begin{aligned} \beta(\underline{q}) = & -\frac{\hbar^2}{2} \sum_{i,j} \left\{ \frac{\partial g_{ij}(\underline{q})}{\partial q_i} \sum_{k,l} \zeta_{kl}(\underline{q}) \frac{\partial g_{kl}(\underline{q})}{\partial q_j} + \right. \\ & + \frac{1}{4} g_{ij}(\underline{q}) \left[ \sum_{k,l} \zeta_{kl}(\underline{q}) \frac{\partial^2 g_{kl}(\underline{q})}{\partial q_i \partial q_j} - \sum_{k,l,m,n} \zeta_{kl}(\underline{q}) \zeta_{mn}(\underline{q}) \times \right. \\ & \left. \left. \times \left( \frac{\partial g_{lm}(\underline{q})}{\partial q_i} \frac{\partial g_{kn}(\underline{q})}{\partial q_j} + \frac{\partial g_{kl}(\underline{q})}{\partial q_i} \frac{\partial g_{mn}(\underline{q})}{\partial q_j} \right) \right] \right\}, \end{aligned} \quad (5)$$

is the pseudo-potential or Watson term [69];  $\zeta_{ij}(\underline{q})$  are elements of  $\underline{G}(\underline{q})^{-1}$ .

We have performed calculations [68, 70] which suggest that the pseudo-potential Eq. (5) makes only a small contribution to the vibrational energy levels of polyatomic molecules such as  $\text{HNO}_3$ . For the water molecule this contribution is less than 1.3, 1.0 and 1.9  $\text{cm}^{-1}$  for the fundamental energy levels  $\nu_1$ ,  $\nu_2$  and  $\nu_3$  respectively. With the growth in the size of the molecule and increase in its total mass, the contribution of the pseudo-potential to the vibrational energy levels decreases significantly [68]. Therefore, to simplify and speed-up

the calculations we neglect the contribution of pseudo-potential. Some of this contribution will be incorporate in our final, empirical potential energy surface (PES).

Elements of the  $\underline{G}(\underline{q})$  matrix are, in general, a complicated function of the vibrational coordinates [68]. As an example, Table I gives elements of  $\underline{G}(\underline{q})$  for the stretching and bending (inter-bond angle) modes. The latter in the case of  $\text{HNO}_3$  are the angles  $\angle \text{N-O-N}$  and  $\text{N-O-H}$ . The elements of  $\underline{G}(\underline{q})$  are presented for two cases: for the bending coordinates given in the form of  $\varphi = -\Delta \arccos\left(\frac{\vec{r}_1 \vec{r}_2}{r_1 r_2}\right)$ , and in the form of its cosine,  $\varphi = -\Delta\left(\frac{\vec{r}_1 \vec{r}_2}{r_1 r_2}\right)$ . In total for  $\text{HNO}_3$  there are 55 elements of  $\underline{G}(\underline{q})$ .

TABLE I: Elements of the  $\underline{G}(\underline{q})$  matrix for two classes of nonlinear bending coordinate  $\varphi$ , where  $m_1$ ,  $m_2$  and  $m_3$  are the atomic masses,  $r_1$  is the length of the bond between atoms 1 and 3 and  $r_2$  the length of the bond between atoms 2 and 3.

	$\varphi = -\Delta \arccos\left(\frac{\vec{r}_1 \vec{r}_2}{r_1 r_2}\right)$	$\varphi = -\Delta\left(\frac{\vec{r}_1 \vec{r}_2}{r_1 r_2}\right)$
$g_{r_1 r_1}$	$\left(\frac{1}{m_1} + \frac{1}{m_3}\right)$	$\left(\frac{1}{m_1} + \frac{1}{m_3}\right)$
$g_{r_2 r_2}$	$\left(\frac{1}{m_2} + \frac{1}{m_3}\right)$	$\left(\frac{1}{m_2} + \frac{1}{m_3}\right)$
$g_{r_1 r_2} = g_{r_2 r_1}$	$\frac{\cos(\varphi)}{m_3}$	$\frac{\varphi}{m_3}$
$g_{r_1 \varphi} = g_{\varphi r_1}$	$\frac{\sin(\varphi)}{r_2 m_3}$	$\frac{(1-\varphi^2)}{r_2 m_3}$
$g_{r_2 \varphi} = g_{\varphi r_2}$	$\frac{\sin(\varphi)}{r_1 m_3}$	$\frac{(1-\varphi^2)}{r_1 m_3}$
$g_{\varphi \varphi}$	$\frac{1}{r_1^2} \frac{m_1+m_3}{m_1 m_3} + \frac{1}{r_2^2} \frac{m_2+m_3}{m_2 m_3} + \frac{2[(\cos(\varphi))^2 - \cos(\varphi)]}{(\sin(\varphi))^2 r_1 r_2 m_3}$	$\frac{(1-\varphi^2)}{r_1^2} \frac{m_1+m_3}{m_1 m_3} + \frac{(1-\varphi^2)}{r_2^2} \frac{m_2+m_3}{m_2 m_3} + \frac{2(\varphi^2 - \varphi)}{r_1 r_2 m_3}$

As can be seen from table I, expressing the bending coordinates as a change in the angle leads to a simplified expression for the matrix elements of  $\underline{G}(\underline{q})$  because their dependence on  $\varphi$  is a linear or quadratic. However, in general  $\underline{G}(\underline{q})$  is a complicated function of the internal coordinates. General expressions of its elements are given elsewhere [68]. In general terms, if both coordinates represent changes in bond lengths then

$$g_{ij}(\underline{q}) = g_{ij}^0(\underline{\varphi}) ; \quad (6)$$

if one coordinate represents a change in the bond length and the second is an angular coordinate then

$$g_{ij}(\underline{q}) = \sum_k \frac{1}{r_k} g_{ij}^k(\underline{\varphi}) , \quad (7)$$

and if both represent angular coordinates it becomes

$$g_{ij}(\underline{q}) = \sum_{k,l} \frac{1}{r_k r_l} g_{ij}^{kl}(\underline{\varphi}) . \quad (8)$$

In these expressions  $r_k$  is bond length of the  $k$ -th bond and  $\underline{\varphi}$  represents the angular coordinates.

$\underline{G}(\underline{q})$  is computed using a second-order Taylor expansion in the angular coordinates

$$g_{ij}(\underline{q}) = g_{ij}^0(0) + \sum_m \left( \frac{\partial g_{ij}^0(\underline{\varphi})}{\partial \varphi_m} \right)_0 \varphi_m + \frac{1}{2} \sum_{m,n} \left( \frac{\partial^2 g_{ij}^0(\underline{\varphi})}{\partial \varphi_m \partial \varphi_n} \right)_0 \varphi_m \varphi_n \quad , \quad (9)$$

for the case where  $i$  and  $j$  both represent bonds;

$$g_{ij}(\underline{q}) = \sum_k \frac{1}{r_k} \left[ g_{ij}^k(0) + \sum_m \left( \frac{\partial g_{ij}^k(\underline{\varphi})}{\partial \varphi_m} \right)_0 \varphi_m + \frac{1}{2} \sum_{m,n} \left( \frac{\partial^2 g_{ij}^k(\underline{\varphi})}{\partial \varphi_m \partial \varphi_n} \right)_0 \varphi_m \varphi_n \right] \quad , \quad (10)$$

for the case of one bond and one bond length;

$$g_{ij}(\underline{q}) = \sum_{k,l} \frac{1}{r_k r_l} \left[ g_{ij}^{kl}(0) + \sum_m \left( \frac{\partial g_{ij}^{kl}(\underline{\varphi})}{\partial \varphi_m} \right)_0 \varphi_m + \frac{1}{2} \sum_{m,n} \left( \frac{\partial^2 g_{ij}^{kl}(\underline{\varphi})}{\partial \varphi_m \partial \varphi_n} \right)_0 \varphi_m \varphi_n \right] \quad . \quad (11)$$

for two angles. It is beneficial to choose an internal coordinate in  $\underline{\varphi}$  as cosine differences  $q_i = \cos \varphi_i - \cos \varphi_i^e$ , where  $\cos \varphi_i^e$  is the instantaneous equilibrium angle for bond angles. As can be seen from Table I, these expansions in terms of  $\underline{\varphi}$  are exact as  $g_{ij}^0(\underline{\varphi})$ ,  $g_{ij}^k(\underline{\varphi})$  and  $g_{ij}^{kl}(\underline{\varphi})$  are quadratic functions of the angular coordinates. In this expansion, a sine difference  $q_i = \sin \varphi_i - \sin \varphi_i^e$  is the obvious choice for an internal coordinate describing a dihedral mode.

To simplify the calculation of the vibrational Hamiltonian matrix elements in block 2 (see below), which correspond to the perturbative contribution for the matrix elements from the main block 1 (see below), the vibrational kinetic energy coefficients are expanded in the polynomial form and truncated at the second order

$$g_{ij}(\underline{q}) = g_{ij}(0) + \sum_m \left( \frac{\partial g_{ij}(\underline{q})}{\partial q_m} \right)_0 q_m + \frac{1}{2} \sum_{m,n} \left( \frac{\partial^2 g_{ij}(\underline{q})}{\partial q_m \partial q_n} \right)_0 q_m q_n \quad . \quad (12)$$

This form is convenient because it allows faster, by an order-of-magnitude or more, computation of the coefficients without significant loss of accuracy.

The potential energy function used by us is a fourth-order polynomial

$$V(\underline{q}) = \frac{1}{2} \sum_{i,j} D_{ij} x_i x_j + \frac{1}{6} \sum_{i,j,k} D_{ijk} x_i x_j x_k + \frac{1}{24} \sum_{i,j,k,l} D_{ijkl} x_i x_j x_k x_l \quad , \quad (13)$$

where Morse coordinates,  $x_i = (1 - \exp^{-\alpha_i \Delta r_i})$ , are used to represent changes of all bonds for  $\text{HNO}_3$  molecule and  $x_i = q_i$  for angular coordinates.

### III. METHOD

For ease of use and better convergence of the basis functions, the  $\chi_i$  are generally chosen to form a complete orthonormal set. In variational calculations of vibrational energy levels,

the Hamiltonian matrix elements are computed using the product form

$$\chi_{kn} = \prod_i \phi_{k_i}(r_i) \prod_s \psi_{n_s}(Q_s) \quad (14)$$

of the basis functions, which are eigenfunctions of the Morse or harmonic oscillators. Morse oscillator functions,  $\phi_{k_i}(r_i)$ , are used for the stretching coordinates,  $r_i$ , for which the potential is given using a Morse coordinate. Harmonic basis functions,  $\psi_{n_s}(Q_s)$ , are used for the other coordinates, which are represented using curvilinear normal coordinates

$$Q_s = \sum_i L_{is}^q q_i \quad (15)$$

expressed as a linear sum over the internal coordinates,  $q_i$ , for which the potential function is defined as a Taylor series. The coordinates  $Q_s$  are those which diagonalize the harmonic part of the Hamiltonian given in the internal coordinates  $q_i$ . With these definitions, all multi-dimensional integrals required to calculate the Hamiltonian matrix elements are separated into products of one-dimensional integrals between either Morse functions or harmonic oscillators. All these integrals have a simple analytic form which results in high-speed computation of the Hamiltonian matrix elements.

The vibrational Hamiltonian matrix constructed in this way is then diagonalized to give the vibrational energy levels  $E_\lambda^{vib}$  and the corresponding wave functions  $\phi_\lambda^{vib}$ .

Our implementation relies on the particular structure of the Hamiltonian matrix ordered by increasing polyad (total vibrational excitation) number,  $N_V$

$$N_V = \sum_{m=1}^{N_c} a_m v_m \quad (16)$$

where  $a_m$  is some weighting which is often roughly proportional to the inverse of the frequency [71]. For simplicity in this work we use  $a_m = 1$  for all  $m$ . This gives the size of the basis set,  $M_B^{\max}$  in terms of the maximum polyad number,  $N_V^{\max}$ ,

$$M_B^{\max} = \frac{(N_V^{\max} + N_c)!}{N_V^{\max}! N_c!} = \prod_{i=1}^{N_c} (N_V^{\max} + i)/i. \quad (17)$$

Calculating all  $N_V \leq N_V^{\text{target}}$  vibrational term values for  $\text{HNO}_3$  with an accuracy better than  $0.3 \text{ cm}^{-1}$  requires basis functions with  $N_V^{\max} \geq N_V^{\text{target}} + 9$ . This means that the Hamiltonian matrix must include all the basis functions for which the difference in  $v_m$  is larger than 9. Thus, an accurate calculation of the fourth overtones and combination frequencies ( $N_V^{\text{target}} = 5$ ) demands a variational basis for  $\text{HNO}_3$  ( $N_c = 9$ ) which includes  $M_B^{\max} = 817\,190$  basis functions.

We use a hybrid variational-perturbation method for calculating ro-vibrational energy levels of a polyatomic molecules [67]. It combines the advantages of both variational calculations and perturbation theory. The vibrational problem is solved by diagonalizing a



For ro-vibrational energy levels it is necessary to calculate elements of the complex Hermitian Hamiltonian matrix

$$H_{\lambda km, \lambda' k' m'}^{JJ'} = \langle \chi_{\lambda km}^J | \hat{H}_{vr} | \chi_{\lambda' k' m'}^{J'} \rangle, \quad (21)$$

using the basis functions

$$\chi_{\lambda km}^J = \Phi_{\lambda}^{vib} \phi_{km}^J, \quad \phi_{km}^J = \left( \frac{2J+1}{8\pi^2} \right)^{1/2} D_{km}^{J*}, \quad (22)$$

where  $D_{km}^J$  is a (complex) Wigner function. In this case

$$H_{\lambda k, \lambda' k'}^J = E_{\lambda}^{vib} \delta_{\lambda \lambda'} \delta_{kk'} - \frac{\hbar^2}{2} \sum_{a,b} \bar{\mu}_{ab}^{\lambda \lambda'} \langle \phi_{km}^J | \frac{\partial^2}{\partial \xi_a \partial \xi_b} | \phi_{k'm'}^J \rangle. \quad (23)$$

The vibrationally averaged moment of inertia,  $\bar{\mu}_{ab}^{\lambda \lambda'}$ , is expanded to second-order as a Taylor series

$$\begin{aligned} \bar{\mu}_{ab}^{\lambda \lambda'} &= \langle \Phi_{\lambda}^{vib} | \mu_{ab}(q) | \Phi_{\lambda'}^{vib} \rangle = \\ &= \mu_{ab}(0) \delta_{\lambda \lambda'} + \sum_m \left( \frac{\partial \mu_{ab}(q)}{\partial q_m} \right)_0 \langle \Phi_{\lambda}^{vib} | q_m | \Phi_{\lambda'}^{vib} \rangle + \frac{1}{2} \sum_{m,n} \left( \frac{\partial^2 \mu_{ab}(q)}{\partial q_m \partial q_n} \right)_0 \langle \Phi_{\lambda}^{vib} | q_m q_n | \Phi_{\lambda'}^{vib} \rangle \end{aligned} \quad (24)$$

and all the integrals reduce to products of one-dimensional integrals over either Morse or harmonic oscillators.

The off-diagonal elements of the vibration-rotation Hamiltonian matrix

$$H_{\lambda k, \lambda' k'}^J = -\frac{\hbar^2}{2} \sum_{a,b} \bar{\mu}_{ab}^{\lambda \lambda'} \langle \phi_{km}^J | \frac{\partial^2}{\partial \xi_a \partial \xi_b} | \phi_{k'm'}^J \rangle \delta_{JJ'}, \quad (25)$$

differ significantly in magnitude, depending on whether they are diagonal in the vibrations,  $\lambda = \lambda'$ , or couple different vibrational states,  $\lambda \neq \lambda'$ .

When calculating the vibrational-rotational energy levels, the off-diagonal elements  $H_{\lambda k, \lambda' k'}^J$  corresponding to different vibrational states  $\lambda \neq \lambda'$  give a much smaller contribution (change in the diagonal elements in the block that will be diagonalized) to the calculated energy levels than the off-diagonal elements  $H_{\lambda k, \lambda k'}^J$  within the vibrational state in question. These changes are given approximately by

$$\Delta E_{\lambda \lambda'} = \frac{(H_{\lambda k, \lambda' k'}^J)^2}{H_{\lambda' k', \lambda' k'}^J - H_{\lambda k, \lambda k}^J}, \quad (26)$$

$$\Delta E_{\lambda \lambda} = \frac{(H_{\lambda k, \lambda k'}^J)^2}{H_{\lambda k', \lambda k'}^J - H_{\lambda k, \lambda k}^J}. \quad (27)$$

However,

$$|H_{\lambda' k', \lambda' k'}^J - H_{\lambda k, \lambda k}^J| \gg |H_{\lambda k', \lambda k'}^J - H_{\lambda k, \lambda k}^J| \quad (28)$$



since  $(H_{\lambda k', \lambda k'}^J - H_{\lambda k, \lambda k}^J)$  involves only a change in the rotational energy level, while  $(H_{\lambda' k', \lambda' k'}^J - H_{\lambda k, \lambda k}^J)$  involves also a change in the vibrational energy level. For semi-rigid molecules with small values of the vibrational quantum numbers the following condition usually holds

$$|H_{\lambda k, \lambda k'}^J| \approx |H_{\lambda k, \lambda' k'}^J| \quad , \quad \lambda \neq \lambda', \quad (29)$$

which results from the slight change in the effective geometry of the molecule upon vibrational excitation. This feature of the vibrational-rotational Hamiltonian matrix is common for large molecules and underpins the ro-vibrational version of our hybrid approach [67]. Again we use second-order perturbation theory, as defined by a Jacobi rotation, to transform the  $H_{\lambda k, \lambda' k'}^J$  matrix to a series of much smaller rotational sub-matrices corresponding to different vibrational states  $\lambda$ ,  $\tilde{H}_{\lambda k, \lambda k'}^J$ . The dimension of each rotational sub-block is  $(2J+1)$  only and we consider  $M_B^{\text{target}}$  sub-matrices that correspond to  $M_B^{\text{target}}$  vibrational states.

As above, we employ a single Jacobi rotation which we apply to the ro-vibrational Hamiltonian. The best agreement with the variational solution is achieved when both the diagonal and off-diagonal elements are updated [67] as given by

$$\tilde{H}_{\lambda k, \lambda k}^J = H_{\lambda k, \lambda k}^J + \sum_{\lambda' \in M_B^{\text{vib}}, \lambda' \neq \lambda} \sum_{k'} t_{\lambda k, \lambda' k'} \eta_{\lambda k, \lambda' k'} \quad (30)$$

for the diagonal elements

$$\begin{aligned} \tilde{H}_{\lambda k, \lambda k''}^J = \frac{1}{2} \sum_{\lambda' \in M_B^{\text{vib}}, \lambda' \neq \lambda} \sum_{k'} & \left[ c_{\lambda k, \lambda' k'} H_{\lambda k, \lambda k''}^J + c_{\lambda k'', \lambda' k'} H_{\lambda k, \lambda k''}^{*J} + \right. \\ & \left. + s_{\lambda k, \lambda' k'} H_{\lambda' k', \lambda k''}^J + s_{\lambda' k', \lambda k''} H_{\lambda k, \lambda' k'}^J \right], \end{aligned} \quad (31)$$

which is a symmetrized version of the standard formula for the single Jacobi rotation with respect to the indices  $\lambda k$  and  $\lambda k''$ . For the off-diagonal elements

$$\begin{aligned} c_{\lambda k, \lambda' k'} &= \frac{1}{\sqrt{1 + t_{\lambda k, \lambda' k'}^2}} \quad , \\ s_{\lambda k, \lambda' k'} &= \frac{c_{\lambda k, \lambda' k'} t_{\lambda k, \lambda' k'}}{\eta_{\lambda k, \lambda' k'}} H_{\lambda k, \lambda' k'}^J \quad , \\ t_{\lambda k, \lambda' k'} &= \text{sign}(\vartheta_{\lambda k, \lambda' k'}) / (|\vartheta_{\lambda k, \lambda' k'}| + \sqrt{1 + \vartheta_{\lambda k, \lambda' k'}^2}) \quad , \\ \eta_{\lambda k, \lambda' k'} &= \text{sign} [\text{Re}(H_{\lambda k, \lambda' k'}^J)] |H_{\lambda k, \lambda' k'}^J| \quad , \\ \vartheta_{\lambda k, \lambda' k'} &= \frac{H_{\lambda k, \lambda k}^J - H_{\lambda' k', \lambda' k'}^J}{2\eta_{\lambda k, \lambda' k'}} \quad , \end{aligned}$$

where  $\underline{H}^J$  and  $\tilde{\underline{H}}^J$  are the initial (unperturbed) matrix and perturbed matrix, respectively;  $\lambda$  runs from 1 to  $M_B^{\text{target}}$ , and  $k = -J \dots + J$ .

The resulting block-diagonal form is then diagonalized for each  $\lambda$  sub-matrix separately. Thus our algorithm replaces the diagonalization of a huge  $[M_B^{\text{vib}} \times (2J+1)]$ -dimensional ro-vibrational matrix with a number of diagonalizations of much smaller dimensional- $[(2J+1)]$  matrices.

#### IV. POTENTIAL ENERGY AND DIPOLE MOMENT FUNCTIONS

An important factor in solving the anharmonic vibrational problem is the choice of internal curvilinear vibrational coordinates,  $q_i$ . This choice determines how close the truncated polynomial potential function of Eq. (13) is to the real PES of the molecule, as well as the specific form of the kinetic energy coefficients matrix,  $\underline{G}(\underline{q})$ , see Eqs. (9), (10) and (11).

The structure of the  $\text{HNO}_3$  molecule and the atom numbering we use is shown in Fig. 2. For  $\text{HNO}_3$  we employ the following vibrational coordinates:

- Four coordinates represent changes in the length of valence bonds between atoms

$$\Delta r_i = \{\Delta r_{\text{NO}_a}, \Delta r_{\text{NO}_b}, \Delta r_{\text{NO}_c}, \Delta r_{\text{O}_c\text{H}}\} ,$$

where

$$r_i = \{r_{\text{NO}_a}, r_{\text{NO}_b}, r_{\text{NO}_c}, r_{\text{O}_c\text{H}}\}$$

are lengths of the bond vectors

$$\vec{r}_i = \{\vec{r}_{\text{NO}_a}, \vec{r}_{\text{NO}_b}, \vec{r}_{\text{NO}_c}, \vec{r}_{\text{O}_c\text{H}}\}$$

with the vectors pointing from the first to the second atom.

- Four coordinates represent changes in the cosines of angles between the valence bonds

$$\varphi_m = \left\{ -\Delta \left( \frac{\vec{r}_{\text{NO}_a} \vec{r}_{\text{NO}_b}}{r_{\text{NO}_a} r_{\text{NO}_b}} \right), -\Delta \left( \frac{\vec{r}_{\text{NO}_a} \vec{r}_{\text{NO}_c}}{r_{\text{NO}_a} r_{\text{NO}_c}} \right), -\Delta \left( \frac{\vec{r}_{\text{NO}_b} \vec{r}_{\text{NO}_c}}{r_{\text{NO}_b} r_{\text{NO}_c}} \right), -\Delta \left( \frac{\vec{r}_{\text{NO}_c} \vec{r}_{\text{O}_c\text{H}}}{r_{\text{NO}_c} r_{\text{O}_c\text{H}}} \right) \right\} .$$

which contain one dependent or redundant angle. This dependence is removed upon the introduction of  $Q_s$  coordinates, see Eq. (15).

- A coordinate corresponding to the change in the sine of the angle between the orientation of bond  $\text{NO}_c$  from the plane formed by bonds  $\text{NO}_a$  and  $\text{NO}_b$

$$\varphi_f = \Delta \left[ \frac{\vec{r}_{\text{NO}_c} (\vec{r}_{\text{NO}_a} \times \vec{r}_{\text{NO}_b})}{r_{\text{NO}_c} r_{\text{NO}_a} r_{\text{NO}_b}} \right] ,$$

- A coordinate corresponding to the change in the sine of the angle between the plane formed by bonds  $\text{NO}_a$ ,  $\text{NO}_b$  and the plane formed by bonds  $\text{NO}_c$ ,  $\text{O}_c\text{H}$  while rotating them relative to each other around  $\text{NO}_c$  bond

$$\varphi_\rho = \Delta \left\{ \frac{\vec{\rho} [(\vec{r}_{\text{NO}_a} \times \vec{r}_{\text{NO}_b}) \times (\vec{r}_{\text{NO}_c} \times \vec{r}_{\text{O}_c\text{H}})]}{r_{\text{NO}_a} r_{\text{NO}_b} r_{\text{NO}_c} r_{\text{O}_c\text{H}}} \right\} .$$

where  $\vec{\rho}$  is a unit vector perpendicular to the equilibrium plane of the molecule.

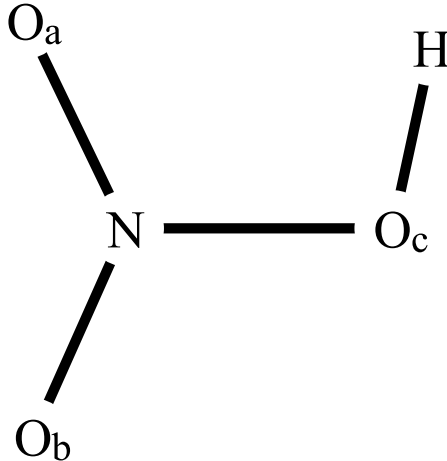


FIG. 2: Structure of the  $\text{HNO}_3$  molecule.

This physically-motivated choice of internal curvilinear vibrational coordinates ensures that quartic expansion of the potential, Eq. (13), stays close to the real PES in the region around the minimum. For example,  $\text{HNO}_3$  has a low frequency mode,  $\nu_9$ , corresponding to rotation of the  $\text{O}_c\text{H}$  bond around the  $\text{NO}_c$  bond which is approximately represented by the coordinate  $\varphi_\rho$ . This vibrational mode is characterized by very large anharmonicity, as it has large amplitude and a strongly anharmonic potential function. Quantum-chemical calculations carried out by Lauvergnat and Nauts [58] show that this rotation corresponds to the potential curve which is close to a sine wave. Our quantum-chemical calculations show that in the expansion of the PES as a function of coordinate  $\varphi_\rho$  in Eq. (13) gives a nonzero quadratic term for coordinate  $\varphi_\rho$  but zero cubic and quartic terms. This is because writing the potential function in the form  $V(\varphi_\rho) = \frac{1}{2}D_{\varphi_\rho\varphi_\rho}\varphi_\rho^2$  is equivalent to defining it as a sine wave in the angle of rotation of the  $\text{O}_c\text{H}$  bond. Thus, choosing the vibrational coordinates in the form of change of sine of the angle for this mode provides a compact definition of the strongly anharmonic sinusoidal potential function as a single term in the expansion Eq. (13). As a result, we obtain good agreement between the experimental and calculated vibrational terms values for  $n\nu_9$  using our *ab initio* potential parameter, see Table II. This in turn means that the calculated spectrum reproduces the absorption intensities for the hot bands starting from the  $\nu_9$ ,  $2\nu_9$ ,  $3\nu_9$  states which are shifted from the main absorption bands and which are characteristic of  $\text{HNO}_3$ , see Figure 5 and discussion below.

We use a simplified method for the initial calculation of parameters for the PES and dipole moment function (DMF). This simplification is justified because our neglect of the pseudo-potential as well as other small contributions such as adiabatic effects [74] means that we cannot calculate energy levels *ab initio* with the accuracy needed to compute a final line list. Therefore, it is necessary to improve the PES and DMF by solving the inverse spectral problem.

TABLE II: Experimental (Exp.) [28] and calculated (Calc.) vibrational term values for excitation of the  $\nu_9$  mode using *ab initio* potential parameters; the result of Lauvergnat and Nauts [58] are given for comparison

Transition	Frequency (cm <sup>-1</sup> )		
	Exp.	Calc. [58]	Our calc.
$\nu_9$	458.2	458.0	456.7
$2\nu_9$	896.3	886.6	894.1
$3\nu_9$	1289.0	1293.1	1284.2
$4\nu_9$	1664.7	1671.9	1656.7

First, we compute a force constant expansion for the PES using a fourth-order Taylor series

$$V(\underline{q}) = \frac{1}{2} \sum_{i,j} f_{ij}^0 q_i q_j + \frac{1}{6} \sum_{i,j,k} f_{ijk}^0 q_i q_j q_k + \frac{1}{24} \sum_{i,j,k,l} f_{ijkl}^0 q_i q_j q_k q_l \quad (32)$$

in internal curvilinear coordinates  $q_i$ . Initial values for the quadratic force constants  $f_{ij}^0$  were calculated using the central finite difference relations

$$f_{ii}^0 = \frac{E^+ + E^- - 2E^0}{\delta q_i^2} \quad , \quad f_{ij}^0 = \frac{E^{++} + E^{--} - E^{+-} - E^{-+}}{4\delta q_i \delta q_j} \quad (33)$$

where  $E^0$  is the molecular energy of the equilibrium configuration and  $E^\pm$  is the energy of the geometry in which the vibrational coordinate  $q_i$  is increased/decreased by  $\delta q_i$ .  $E^{++}$ ,  $E^{--}$ ,  $E^{+-}$ ,  $E^{-+}$  are energies for geometries in which the vibrational coordinates  $q_i$  and  $q_j$  are increased and/or decreased by multiples of  $\delta q_i$  and  $\delta q_j$ . Energies and the equilibrium geometry of HNO<sub>3</sub> were calculated *ab initio* at the CCSD(T)/aug-cc-pVQZ level of theory using MOLPRO [75]. Similarly, the initial values of cubic  $f_{ijk}^0$  and quartic  $f_{ijkl}^0$  force constants were calculated using the finite difference relations

$$f_{ijk}^0 = \frac{f_{ij}^+ + f_{ij}^- - 2f_{ij}^0}{\delta q_k^2} \quad , \quad f_{ijkl}^0 = \frac{f_{ij}^{++} + f_{ij}^{--} - f_{ij}^{+-} - f_{ij}^{-+}}{4\delta q_k \delta q_l} \quad (34)$$

where  $f_{ij}^0$  are the Hessian (quadratic force constants) at the equilibrium geometry,  $f_{ij}^\pm$  is the Hessian corresponding to an increase/decrease in the vibrational coordinates  $q_i$  by  $\delta q_i$ . The Hessians  $f_{ij}^{++}$ ,  $f_{ij}^{--}$ ,  $f_{ij}^{+-}$ ,  $f_{ij}^{-+}$  are computed at geometries obtained by increasing and decreasing vibrational coordinates  $q_i$  and  $q_j$  by multiples of  $\delta q_i$  and  $\delta q_j$ . These Hessians were calculated *ab initio* at the MP2/aug-cc-pVQZ level of theory using Gaussian [76]. These calculations were based on the MP2/aug-cc-pVQZ equilibrium geometry.

The second step of the calculation uses the initial force constants  $f_{ij}^0$ ,  $f_{ijk}^0$ ,  $f_{ijkl}^0$  to construct the constants  $D_{ij}$ ,  $D_{ijk}$ ,  $D_{ijkl}$  which are used to represent the PES, see Eq. (32). This requires taking into account the relation between the  $f$ ,  $D$  and  $\alpha$  constants for the Morse oscillator, for example,  $f_{ii}^0 = D_{ii}\alpha_i^2$ .

In the third stage of the calculation the PES parameters are refined using the empirical values of the energy levels. Solution of the inverse spectral problem is facilitated by the analytic evaluation of the first derivatives of the energy levels,  $E_i$ , with respect to PES parameters  $D_j$  using the Hellmann-Feynman theorem:

$$\frac{\partial E_i}{\partial D_j} = \langle \psi_i | \frac{\partial \hat{H}_v}{\partial D_j} | \psi_i \rangle = \langle \psi_i | \frac{\partial V(\underline{q})}{\partial D_j} | \psi_i \rangle \quad (35)$$

where  $\psi_i$  is the wave function of energy level  $E_i$ .

Our solution of the inverse spectral problem is based on the method of regularization due to Tikhonov [77, 78]. This method minimizes the functional

$$\Phi = \sum_i (E_i^c - E_i^e)^2 W_i + \sum_j \left[ \alpha_j \left( \frac{D_j - D_j^0}{\Delta D_j^{max}} \right)^2 + \beta_j \left( \frac{D_j - D_j^0}{\Delta D_j^{max}} \right)^{10} \right]. \quad (36)$$

where  $E_i^c$ ,  $E_i^e$  and  $W_i$  are the calculated and experimental values of the energy level and its weight,  $D_j$  and  $D_j^0$  are the current and initial values of the parameters, and  $\Delta D_j^{max}$  is the maximum possible deviation of parameter value from its initial value. In this formula,  $\alpha_j$  and  $\beta_j$  are regularization parameters that allow one to control progress in solving the inverse problem. The terms containing  $D_j$  in this functional allows one to constrain the refined parameters to their initial (*ab initio*) values. The method of regularization ensures that there is always a valid solution, even when the number of experimental energies is less than the number of variable parameters. This is similar to the method where the shape of the potential functions are controlled by constraining directly to the *ab initio* energies (see, for example, [79]).

The dipole moment of  $\text{HNO}_3$  is represented as a second-order polynomial

$$\vec{D}(\underline{q}) = \vec{D}^0 + \sum_i \vec{d}_i q_i + \frac{1}{2} \sum_{i,j} \vec{d}_{ij} q_i q_j, \quad (37)$$

where  $\vec{D}^0$  is the equilibrium value of the dipole moment,  $\vec{d}_i$  and  $\vec{d}_{ij}$  equal, respectively, the first and second derivatives of the dipole moment with respect to the curvilinear coordinates  $q_i$  and  $q_j$ . Initial values of  $\vec{d}_i$  and  $\vec{d}_{ij}$  were calculated using the finite difference relations

$$\vec{d}_i = \frac{\vec{D}^+ + \vec{D}^- - 2\vec{D}^0}{\delta q_i^2}, \quad \vec{d}_{ij} = \frac{\vec{D}^{++} + \vec{D}^{--} - \vec{D}^{+-} - \vec{D}^{-+}}{4\delta q_i \delta q_j}, \quad (38)$$

where  $\vec{D}^\pm$  is the dipole moment corresponding to an increase/decrease in the vibrational coordinates  $q_i$  by  $\delta q_i$ . Dipole moments  $\vec{D}^{++}$ ,  $\vec{D}^{--}$ ,  $\vec{D}^{+-}$ ,  $\vec{D}^{-+}$  correspond to the geometries obtained by increasing or decreasing vibrational coordinates  $q_i$  and  $q_j$  by multiples of  $\delta q_i$  and  $\delta q_j$ . Dipole moments were calculated *ab initio* at the CCSD(T)/aug-cc-pVQZ level of theory using MOLPRO from the change in energy of the molecule in an external electric field, which is considered the better of the methods for computing *ab initio* dipoles [80].

Calculation of initial values of the PES and DMF parameters and all subsequent calculations were made using program ANGMOL [68]. ANGMOL automatically produces the necessary inputs for MOLPRO and Gaussian, runs these programs and extracts the required data (energy, Hessian and dipole moment) from their listings. These calculations take into account the relationship between our internal curvilinear coordinates,  $q_i$ , and the Cartesian coordinates of the atoms [68].

The calculated initial values of the force constants and the dipole moment of the molecule depends on the increment,  $\delta q_i$ , used to evaluate the derivatives. For small values of  $\delta q_i$ , these derivatives are distorted by the finite numerical precision inherent in Gaussian and MOLPRO, while for large increments the PES and DMF may not be quadratic. We find that optimal increments,  $\delta q_i$ , are 0.01 Å for bonds and 0.01 for changes in cosines and sines of the angular coordinates. These increments were used in all calculations of the initial PES and DMF coefficients.

Ro-vibrational calculations showed that the CCSD(T)/aug-cc-pVQZ equilibrium geometry does not accurately describe the rotational energy levels. Therefore we used a modified geometry in which all bond lengths were reduced by 0.1 %. Table III gives our calculated and modified equilibrium geometry.

TABLE III: Equilibrium bond lengths (Å) and angles (°) in the molecule HNO<sub>3</sub> which is planar.

Parameter	<i>Ab initio</i>	Modified
$r_{NO_a}$	1.21032	1.20911
$r_{NO_b}$	1.19531	1.19412
$r_{NO_c}$	1.39960	1.39820
$r_{O_cH}$	0.96985	0.96888
$\alpha_{NO_a,NO_b}$	130.2713	130.2713
$\alpha_{NO_a,NO_c}$	115.7199	115.7199
$\alpha_{NO_b,NO_c}$	114.0088	114.0088
$\alpha_{NO_c,OH}$	102.2040	102.2040

Finally we note that the program ANGMOL is freely available on upon request to the first author.

## V. CALCULATED VIBRATIONAL TERM VALUES

First the vibrational energy levels were calculated using the Hamiltonian described in Section II and our hybrid variational-perturbation method [67], as implemented in ANGMOL [68].

An important feature of the HNO<sub>3</sub> IR spectrum [28, 43, 81] in the 0 - 7000 cm<sup>-1</sup> range is that absorption is dominated by the fundamental ( $\nu_i$ ), first overtones ( $2\nu_i$ ), and first combination ( $\nu_i + \nu_j$ ) bands. The presence of low-frequency vibrations with high anharmonicity also leads to observation of hot band transitions, such as  $4\nu_i - 3\nu_i$  and  $4\nu_i - 2\nu_i$ , even

at room temperature. The strongest hot-band transitions correspond to those involving the low-frequency  $\nu_9$  mode. In addition, the spectrum is further complicated by strong Fermi resonances, for example between  $\nu_5$  and  $2\nu_9$ .

We aim to make accurate calculations (better than  $1 \text{ cm}^{-1}$ ) for vibrational states with the quantum numbers up to  $N_V^{\text{target}} = 5$  which corresponds to  $M_B^{\text{target}} = 2\,002$  vibrational states. This means we must include in the fully diagonalized block 1 all states with  $N_V^{(1)} \leq 9$  which gives  $M_B^{(1)} = 48\,620$ . The total size of the basis corresponds to  $N_V^{\text{max}} = 14$  and  $N_B^{\text{max}} = 817\,190$  functions. Computing the elements of block 2, whose size is  $M_B^{(1)} \times M_B^{\text{max}} = 48620 \times 817190$ , and including them as a perturbation takes 3 hours on an 8-core desktop computer. This is cheap compared to the subsequent diagonalization of the 48 620 dimensional matrix.

Table IV shows the calculated and experimental vibrational term values for the  $\text{HNO}_3$  molecule. These calculations were carried out with our initial, *ab initio*, PES. As can be seen, this PES gives a generally satisfactory description of the experimental vibrational term values. The average deviation between the calculated and experimental fundamental energy levels is  $3 \text{ cm}^{-1}$ . For the first overtone and combination levels it is  $6 \text{ cm}^{-1}$ . The calculation describes the strong Fermi resonance between  $\nu_5$  and  $2\nu_9$  well.

However, this accuracy is not sufficient to generate a good line list. Therefore, we have refined the PES parameters using the method of regularization. The parameters  $\alpha_i$ , which define the half-width of the Morse functions for the stretching coordinates, were fixed in the fits to their *ab initio* values. The inverse problem was solved in two steps. First the 39 quadratic parameters of the potential function,  $D_{ij}$  of Eq. (13), were refined using the 11 equally-weighted vibrational term values: the fundamentals plus  $2\nu_9$  and  $\nu_6 + \nu_9$ . The results of this fit are given as calculation II in Table IV. The average deviation between calculated and experimental fundamental levels energy is now less than  $0.2 \text{ cm}^{-1}$  and is about  $3 \text{ cm}^{-1}$  for the first overtone and first combination bands.

In the second stage all potential parameters  $D_{ij}$ ,  $D_{ijk}$  and  $D_{ijkl}$  are processed: a total of 584 parameters were refined using the 46 experimental term values, given in Table IV. Following the regularization method we use 584 additional constraints to for these parameters to their initial *ab initio*  $D_{ijk}$  and  $D_{ijkl}$  values and to the values of  $D_{ij}$  obtained at the previous stage. This makes the inverse problem fully determined despite the small amount of experimental data. States with up to 3 quanta of excitation had weight 1.0, while 4 quanta states, whose energies are more uncertain, had a weight of 0.1. The results of this fit are shown as calculation III in Table IV. The average deviation between calculated and experimental fundamental levels energy remains  $0.2 \text{ cm}^{-1}$ , but for the first overtone and first combination bands it is reduced to  $0.4 \text{ cm}^{-1}$ . This potential function was subsequently used to calculate the ro-vibrational energy levels and the line list.

We note that the ‘experimental’ values of the vibrational term values given in Table IV do not match those given by Perrin *et al* [28] or Feierabend *et al* [43]. This is because in these laboratory studies the corresponding vibrational term values were estimated as band centers,

TABLE IV: Experimental and calculated vibrational term values, in  $\text{cm}^{-1}$ , for  $\text{HNO}_3$ . Calculation I is based on the *ab initio* parameters while Calculations II and III are the results of the use of the refined PES values. The references give the source of the experimental data used, but see text for a discussion of the actual values given.

State	I	II	III	Exp.	Source
$A''$ $\nu_9$	456.7	458.2	458.2	458.2	[28]
$A'$ $\nu_8$	577.0	580.3	580.4	580.3	[38]
$A'$ $\nu_7$	647.3	646.7	647.0	646.5	[38]
$A''$ $\nu_6$	770.1	763.2	763.3	763.1	[81]
$A'$ $\nu_5$	876.7	879.1	878.8	879.1	[81]
$A'$ $2\nu_9$	894.1	896.4	896.2	896.3	[81]
$A''$ $\nu_8+\nu_9$	1025.0	1029.9	1038.0	1038.0	[81]
$A''$ $\nu_7+\nu_9$	1096.0	1097.0	1100.3	1100.8	[81]
$A'$ $\nu_6+\nu_9$	1210.2	1205.4	1205.2	1205.6	[81]
$A''$ $3\nu_9$	1284.2	1288.8	1289.6	1289.0	[28]
$A'$ $\nu_4$	1303.0	1302.9	1303.2	1303.1	[81]
$A'$ $\nu_3$	1329.6	1326.2	1326.3	1325.7	[81]
$A''$ $\nu_5+\nu_9$	1337.5	1340.5	1343.7	1343.6	[28]
$A'$ $\nu_7+\nu_5$	1507.9	1509.9	1516.0	1515.9	[81]
$A'$ $2\nu_6$	1539.2	1525.4	1525.4	1525.6	[81]
$A'$ $\nu_7+2\nu_9$	1526.1	1528.2	1533.7	1533.2	[81]
$A'$ $4\nu_9$	1656.7	1662.8	1661.3	1664.7	[28]
$A'$ $\nu_2$	1716.4	1709.5	1709.4	1709.6	[81]
$A'$ $2\nu_5$	1747.1	1751.3	1757.0	1757.0	[81]
$A'$ $\nu_5+2\nu_9$	1769.9	1773.9	1780.4	1780.3	[81]
$A''$ $\nu_3+\nu_9$	1790.2	1788.0	1789.2	1789.7	[81]
$A'$ $\nu_3+\nu_8$	1900.6	1900.4	1905.8	1906.0	[81]
$A'$ $\nu_4+\nu_7$	1941.4	1940.8	1949.2	1949.6	[81]
$A'$ $\nu_3+\nu_7$	1968.4	1964.3	1974.7	1975.2	[81]
$A''$ $\nu_4+\nu_6$	2066.5	2059.7	2061.4	2061.4	[81]
$A''$ $\nu_3+\nu_6$	2102.4	2091.5	2091.9	2092.0	[81]
$A''$ $\nu_2+\nu_9$	2174.5	2169.7	2165.2	2164.8	[81]
$A'$ $\nu_2+\nu_5$	2537.5	2531.0	2530.8	2530.6	[43]
$A'$ $2\nu_4$	2584.2	2582.1	2580.5	2580.9	[43]
$A'$ $\nu_2+2\nu_9$	2595.2	2593.2	2596.2	2596.5	[43]
$A'$ $2\nu_3$	2651.0	2644.0	2643.8	2644.4	[43]
$A'$ $\nu_2+\nu_4$	3003.2	2998.2	2998.4	2998.5	[43]
$A'$ $\nu_2+\nu_3$	3033.3	3022.6	3021.8	3022.1	[43]
$A'$ $2\nu_2$	3411.2	3396.7	3404.2	3404.4	[43]
$A'$ $\nu_1$	3553.3	3551.6	3551.6	3551.9	[81]
$A''$ $\nu_1+\nu_9$	4007.3	4007.3	4006.6	4007.0	[43]
$A'$ $\nu_1+\nu_8$	4125.5	4127.3	4127.4	4127.5	[43]
$A'$ $\nu_1+\nu_7$	4199.4	4196.3	4196.8	4197.0	[43]
$A'$ $2\nu_2+2\nu_9$	4319.1	4314.0	4315.0	4314.5	[43]
$A'$ $\nu_1+\nu_5$	4427.6	4428.2	4427.4	4427.6	[43]
$A'$ $\nu_1+2\nu_9$	4445.5	4446.0	4445.5	4445.8	[43]
$A'$ $2\nu_2+\nu_3$	4757.6	4751.5	4751.9	4750.0	[43]
$A''$ $\nu_1+3\nu_9$	4831.0	4833.4	4833.9	4832.8	[43]
$A'$ $\nu_1+\nu_4$	4870.7	4866.8	4865.5	4866.3	[43]
$A'$ $\nu_1+\nu_2$	5256.6	5248.2	5254.5	5252.4	[43]
$A'$ $2\nu_1$	6941.5	6935.1	6938.8	6940.0	[43]



either as maxima of the Q-branches or minima between the P- and R-branches, and thus do not precisely correspond to the  $J = 0$  energy of the vibrationally excited state, because they also contain some rotational structure. Therefore, Table IV gives our revised values: vibrational term values were determined as the energy, which, after their substitution in a full ro-vibrational calculation, gives coincidence between the computed and experimental rotational structure of the absorption band in question. These values should represent the best available estimate for the  $\text{HNO}_3$  vibrational term values. Our estimated accuracy for the ‘experimental’ vibrational term values given in Table IV is better than  $0.1 \text{ cm}^{-1}$ . The typical difference between our values and those given previously [28, 43] is about  $1 \text{ cm}^{-1}$ , which corresponds to the half-width of a typical Q-branch. Finally, some experimental values given in Table IV do not come from high resolution spectra; these were identified by us from the observed absorption cross sections provided by PNNL [81].

## VI. CALCULATED RO-VIBRATIONAL SPECTRUM

We compute the rotation-vibration spectrum in the range  $0\text{--}7000 \text{ cm}^{-1}$ , which includes all first overtones and first combination bands. To include all hot absorption bands present at room temperature it was necessary to include all vibrational states lying below  $9000 \text{ cm}^{-1}$ .

There are about 20 000 vibrational states below  $9000 \text{ cm}^{-1}$ . Therefore, the calculation of ro-vibrational energy levels for all of these vibrational states and the calculation of intensities of allowed transitions between all the ro-vibrational levels is lengthy, even when using our hybrid method. Initially, this calculation took about 6 months on a 8-core desktop computer. However as described below, this time can be reduced by two orders-of-magnitude by computing only those ro-vibrational energy levels and transition intensities which are actually needed. For concreteness, in what follows we consider the explicit example of the calculation of a room temperature spectrum.

First, room temperature spectrum experiments do not show any significant transitions to vibrational states with the polyad number  $N_V > 4$ , due to the very low intensity of such bands. Therefore, we only need to obtain results for the vibrational states with the polyad number  $N_V^{\text{target}} \leq 4$ . This reduces the number of vibrational states for which ro-vibrational energy levels are required to  $M_B^{\text{target}} = 1\,715$ . All other ro-vibrational states are only used to perturb the target ro-vibrational energy levels.

Second, not all of the 20 000 vibrational states below  $9000 \text{ cm}^{-1}$  actually significantly contribute the target ro-vibrational energy levels. This is because a large difference between the quantum numbers  $v_i^\lambda$  and  $v_i^{\lambda'}$  from vibrational states  $\lambda$  and  $\lambda'$  leads to vanishingly small values of the corresponding matrix elements  $\bar{\mu}_{ab}^{\lambda\lambda'}$ , Eq. (24), and  $H_{\lambda k, \lambda' k'}^J$ , Eq. (23). For example, for purely harmonic basis functions, the matrix elements  $\bar{\mu}_{ab}^{\lambda\lambda'}$  and  $H_{\lambda k, \lambda' k'}^J$  are exactly zero for  $\sum_i |v_i^\lambda - v_i^{\lambda'}| > 2$ . Using a mixed Morse-harmonic basis we obtain  $\bar{\mu}_{ab}^{\lambda\lambda'} \approx 0$  and  $H_{\lambda k, \lambda' k'}^J \approx 0$  for  $\sum_i |v_i^\lambda - v_i^{\lambda'}| > 3$ . Therefore, only the contribution from the vibrational

states with polyad numbers  $N_V^{\text{vib}} \leq 7$  need to be evaluated as perturbation to the target ro-vibrational energy levels from the  $M_B^{\text{vib}}$  vibrational states. In this case,  $M_B^{\text{vib}} = 9\,477$ , which is only about half the vibrational states below  $9000\text{ cm}^{-1}$ . Besides, when summing the perturbation effect for a given ro-vibrational energy levels, we can skip all pairs with  $\sum_i |v_i^\lambda - v_i^{\lambda'}| > 3$ . Therefore, the sums in Eqs. (30) and (31) for each value of  $\lambda$  will run over less than a tenth of all the levels included in  $M_B^{\text{vib}}$ .

Third, when considering a transition between different ro-vibrational states, it is useful to make a preliminary assessment of its intensity. If the estimated value is below some threshold, the intensity calculation can be skipped. Such intensities can be neglected either because of the small intrinsic value of the transition dipole or because of the low population of the initial ro-vibrational energy level caused by the Boltzmann factor. As, in large line lists, computation of the transition intensities dominates the computer time [82], this significantly reduces the overall computer time.

When these three factors are taken into account, the time for computing the ro-vibrational spectrum in the  $0 - 7000\text{ cm}^{-1}$  region is reduced from 6 months to two days on an 8-core desktop computer. This is quick enough even to allow us to refine our *ab initio* DMF by fitting to experimental line intensities, thus improving agreement between observed and computed spectra.

In this case, the DMF parameters  $\vec{D}^0$ ,  $\vec{d}_i$  and  $\vec{d}_{ij}$  of Eq. (37) were varied to achieve the best agreement between theoretical and experimental integrated transition intensities for a given spectral region. This fit was again conducted using the method of regularization. We used experimental cross sections from the PNNL database [81] as input data. In the low-frequency region, which is absent from the PNNL spectrum, we used data from HITRAN [7]. In the high-frequency region  $4200 - 7000\text{ cm}^{-1}$ , where the PNNL spectra are very noisy, we used the experimental intensities of Feierabend *et al* [43]. It should be noted that Feierabend *et al* give only relative intensities, where the  $\nu_1$  band intensity was taken as unity. For this region, Table V gives absolute intensities obtained by multiplying the relative intensities of Feierabend *et al* by the absolute intensity of the  $\nu_1$  band from PNNL. Absolute intensity values for PNNL [81] were obtained by integrating the PNNL absorption cross sections. Whenever possible, we sought not only to have the best agreement between the calculated and experimental integral intensities for a given spectral range, but also good agreement between the intensities of individual transitions within each of the spectral bands. In the case of complex absorption bands, which are formed from the superposition of several intense bands, we used those intensities which gave the best fit between the experimental and calculated shape of the absorption band.

Table V shows experimental and calculated intensities for different frequency regions using the initial (calculation A) and fitted (calculation B) values of the parameters  $\vec{D}^0$ ,  $\vec{d}_i$  and  $\vec{d}_{ij}$  in the DMF. This table shows that the use of the *ab initio* DMF leads to a systematic overestimation of the calculated intensities: by an average of 40% for the fundamentals bands and by 90% for the first overtones and first combination bands. Fitting gives greatly

TABLE V: Experimental and calculated intensities by region for HNO<sub>3</sub>: experimental data is taken from PNNL [81] , HITRAN [7] and Feierabend *et al* [43]. Calculation A used an *ab initio* DMF and calculation B a fitted DMF. The dominant bands for each frequency window are also given.

Band	Frequency (cm <sup>-1</sup> )	Intensity (km/mole)				
		[7]	[81]	[43]	Calc. A	Calc. B
Rotation	0 - 100	6.7			7.2	6.7
Hot	100 - 350				0.15	0.14
$\nu_9$	350 - 520	77.7			107.3	77.7
$\nu_8$	520 - 610	5.7			6.4	5.6
$\nu_7$	610 - 700	5.6			13.2	5.6
$\nu_6$	700 - 830	7.4			6.9	7.4
$\nu_5$ , $2\nu_9$	830 - 950	124.5	110.9		151.4	110.9
$\nu_8+\nu_9$ , $\nu_7+\nu_9$	950 - 1140				0.53	0.82
$\nu_6+\nu_9$	1140 - 1240	5.7	7.9		8.7	7.9
$\nu_4$ , $\nu_3$ , $3\nu_9$ , $\nu_5+\nu_9$	1240 - 1380	229.3	221.6		300.4	220.8
$\nu_7+\nu_5$ , $2\nu_6$ , $\nu_7+2\nu_9$	1380 - 1600		6.5		4.7	6.1
$\nu_2$ , $4\nu_9$ , $2\nu_5$ , $\nu_5+2\nu_9$ , $\nu_3+\nu_9$	1600 - 1825	263.5	251.8		354.0	251.4
$\nu_3+\nu_8$ , $\nu_4+\nu_7$ , $\nu_3+\nu_7$	1825 - 2040		1.5		3.4	1.8
$\nu_3+\nu_5$ , $\nu_2+\nu_9$	2170 - 2240		0.37	0.44	0.67	0.38
$\nu_2+\nu_5$ , $2\nu_4$ , $\nu_2+2\nu_9$ , $2\nu_3$	2460 - 2710		6.2	8.2	8.4	6.1
$\nu_2+\nu_4$ , $\nu_2+\nu_3$	2920 - 3055		6.6	8.2	3.6	6.4
$2\nu_2$	3360 - 3440		1.3	1.6	0.51	1.3
$\nu_1$	3490 - 3610		54.9	54.9	76.9	54.9
$3\nu_4$ , $\nu_3+2\nu_4$	3828 - 3893		0.08	0.11	0.33	0.34
$\nu_1+\nu_9$	3950 - 4050		0.98	1.1	1.9	1.0
$\nu_1+\nu_8$	4075 - 4160		0.19	0.27	0.53	0.35
$2\nu_2+2\nu_9$	4230 - 4355		0.12	0.22	0.61	0.55
$\nu_1+\nu_5$ , $\nu_1+2\nu_9$	4385 - 4490		0.13	0.16	0.20	0.18
$2\nu_2+\nu_3$ , $2\nu_2+\nu_4$	4630 - 4710		0.06	0.27	0.62	0.48
$2\nu_2+\nu_3$	4710 - 4780		0.13	0.11	0.67	0.24
$\nu_1+\nu_4$ , $\nu_1+\nu_3$ , $\nu_1+3\nu_9$	4790 - 4905		0.89	1.0	1.7	1.1
$3\nu_2$	5040 - 5115		0.06	0.05	0.59	0.50
$\nu_1+\nu_2$	5210 - 5290		0.33	0.33	0.52	0.40
$\nu_1+2\nu_4$	6080 - 6195		0.12	0.05	0.85	0.65
$2\nu_1$ , $\nu_1+2\nu_2$	6865 - 7005			2.1	3.0	2.1

improved agreement between the calculated and experimental intensities. In this case, the average difference for the intensities of the fundamental transitions is only 0.3% and for the first overtone and combination bands it is 40%. These differences between the computed and measured band intensities are within the experimental uncertainties. For example in the region of the fundamental bands, intensities from HITRAN are on average 10% higher than the absorption cross sections given by PNNL. At the same time, the intensity of the  $\nu_6+\nu_9$  combination band is 30% less in HITRAN than PNNL. In addition, the PNNL spectrum which we used becomes very noisy for low intensity absorptions. Therefore, at present, it does not make sense to further improve the agreement between calculated and experimental intensities.

Figure 3 compares our calculated spectra for HNO<sub>3</sub> at 296 K with the data from HITRAN.

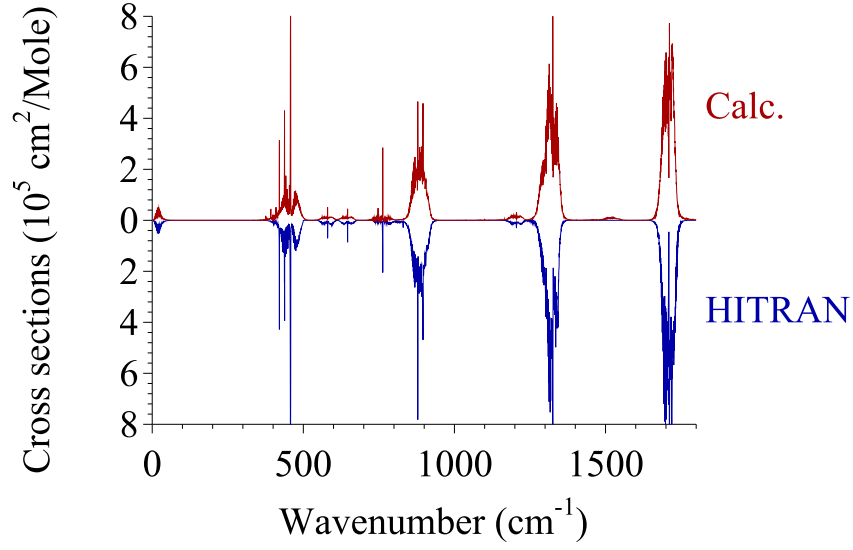


FIG. 3: Calculated (red curve) and HITRAN (blue curve) 296 K  $\text{HNO}_3$  spectra in the 0 - 1800  $\text{cm}^{-1}$  region.

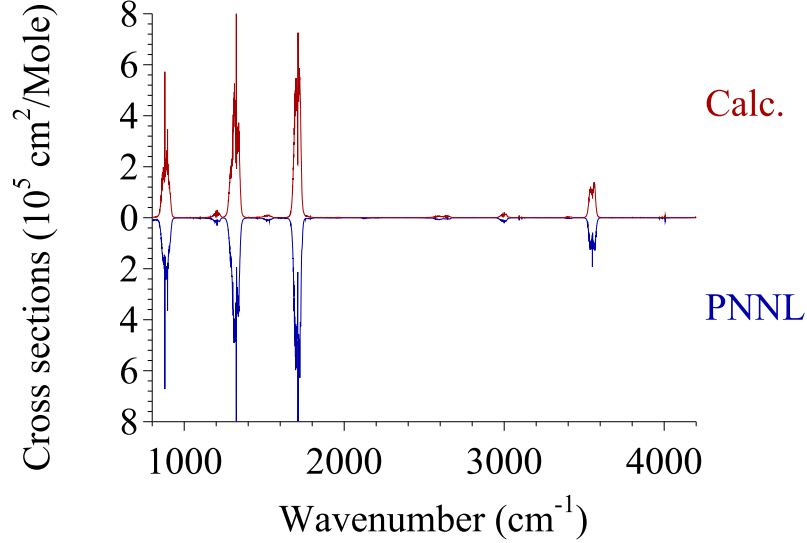


FIG. 4: Calculated (red curve) and experimental PNNL (blue curve) 298 K cross sections in the 800 - 4200  $\text{cm}^{-1}$  region.

Although HITRAN aims to be comprehensive for atmospherically important molecules such as  $\text{HNO}_3$ , it actually contains only a few  $\text{HNO}_3$  vibrational bands which means that HITRAN gives much less complete coverage than the measured cross sections from PNNL. In particular, HITRAN has no data for wavenumbers higher than 1900  $\text{cm}^{-1}$ . Figures 4 give a similar overview comparison of our calculated spectrum with the 298 K PNNL cross sections.

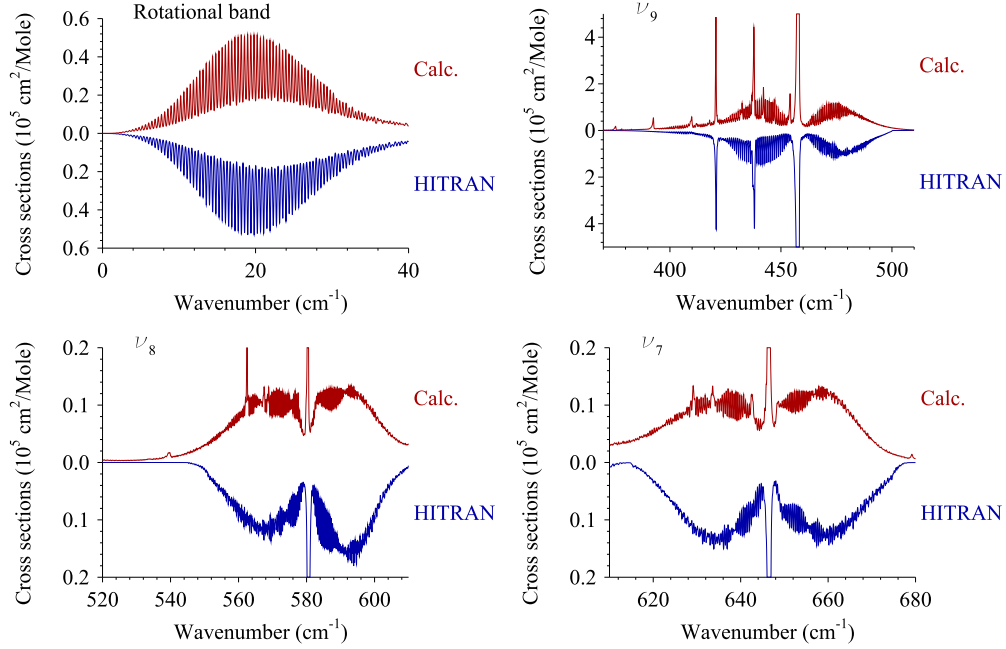


FIG. 5: Comparison of the main bands in HITRAN below  $700\text{ cm}^{-1}$ : calculated (red curve) and HITRAN (blue curve)

Figure 5 presents more detailed comparisons for the main bands in HITRAN below  $700\text{ cm}^{-1}$ . Generally the agreement is very good. HITRAN is systematically missing data on hot bands even when they give rise to strong, sharp features. For example, the  $\nu_9$  band region is missing several, intense hot bands which are found in our calculation and which have been experimentally observed [28]. A similar situation arises for the  $\nu_6$  band, see Fig. 6. This band is the only one for which a direct comparison of HITRAN and PNNL data is possible. Again our calculations predict sharp hot-band features which are absent from the HITRAN spectra. Despite becoming increasingly noisy at low frequencies, the strongest of these hot-band features can clearly be seen in the PNNL cross sections. It should be noted that the anharmonic character of the torsion  $\nu_9$  mode gives rise to a sequence of hot bands in the region  $370\text{--}510\text{ cm}^{-1}$ , significantly shifted from the center of  $\nu_9$ .

Figure 7 presents detailed comparisons of our calculated cross sections with those of PNNL measured at  $T = 298\text{ K}$ . Our spectra were converted to cross sections using a Voigt profile  $\sigma = \gamma = 0.075\text{ cm}^{-1}$  (a half width at half maximum (HWHM) of  $0.153\text{ cm}^{-1}$ ), chosen to match spectra from the PNNL database [81]. As can be seen, our calculated spectrum reproduces the PNNL cross sections very well both in the overall shape and magnitude of the band. This is also true for the finer details of the spectrum. For example, the  $1800\text{--}2000\text{ cm}^{-1}$  region shows many features due to hot bands and combination bands which are generally well-represented in our calculated spectrum.

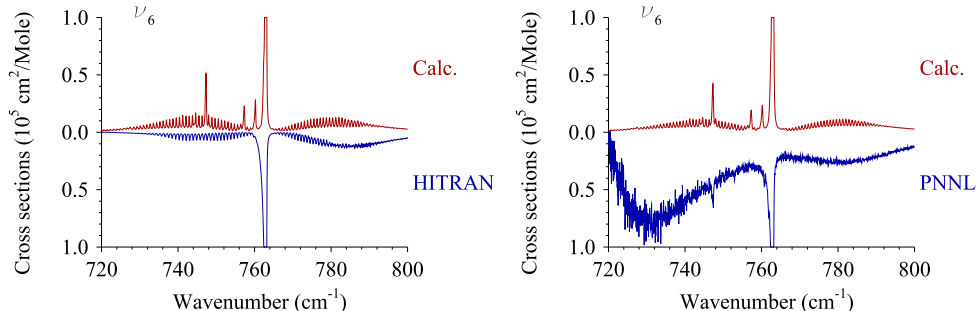


FIG. 6: Comparison of spectra for  $\nu_6$  band regions: Calculated (red curve) and experimental HITRAN/PNNL (blue curve).

## VII. LINE LIST

The data necessary to reproduce the spectrum of  $\text{HNO}_3$  at temperatures up to 300 K in the 0 - 7000  $\text{cm}^{-1}$  range has been stored in a variety of formats. In particular, we have created a line list in the ExoMol format [83, 84]. The list contains transitions involving rotational quantum number  $J$  up to 70 for  $9 \times 10^6$  vibration-rotation energy levels belonging to 1715 vibrational states and associated transitions probabilities, in form of Einstein A coefficients. The rotational angular momentum threshold of  $J = 70$  provides a complete set of rotational energy levels up to 1050  $\text{cm}^{-1}$ . To reduce the very large number of transitions between different ro-vibrational energy levels we only retain those transitions for which the intensity is greater than  $10^{-32}$   $\text{cm}/\text{molecule}$  at 296 K. In total the line list contains about two billion transitions; it can be found on the ExoMol [83] website [www.exomol.com](http://www.exomol.com). Key information on the calculation in form of the initial and refined coefficients of the potential and dipole moment functions can be found in the supplementary data to this article [85].

## VIII. CONCLUSION

We present a detailed study of the infrared spectrum of nitric acid. Calculations are performed using a hybrid variational-perturbation procedure which allows the whole spectrum can be calculated rapidly on a standard desktop computer when combined with the initial guess on the intensities of strong lines provided by experiment. This has allowed us to tune both the potential energy surface and dipole moment function to the available experimental data. Comparison with the experimental compilations available in HITRAN [7] and the PNNL database [81] generally give excellent agreement. However we find that HITRAN is systematically missing features due to hot bands, even when these are rather strong.

$\text{HNO}_3$  has a strong spectral signature in the Earth's atmosphere which can be clearly seen from space. As such it is one of a number of species that are considered to be possible signatures of life (biosignature). To help aid the detection of life outside the solar system

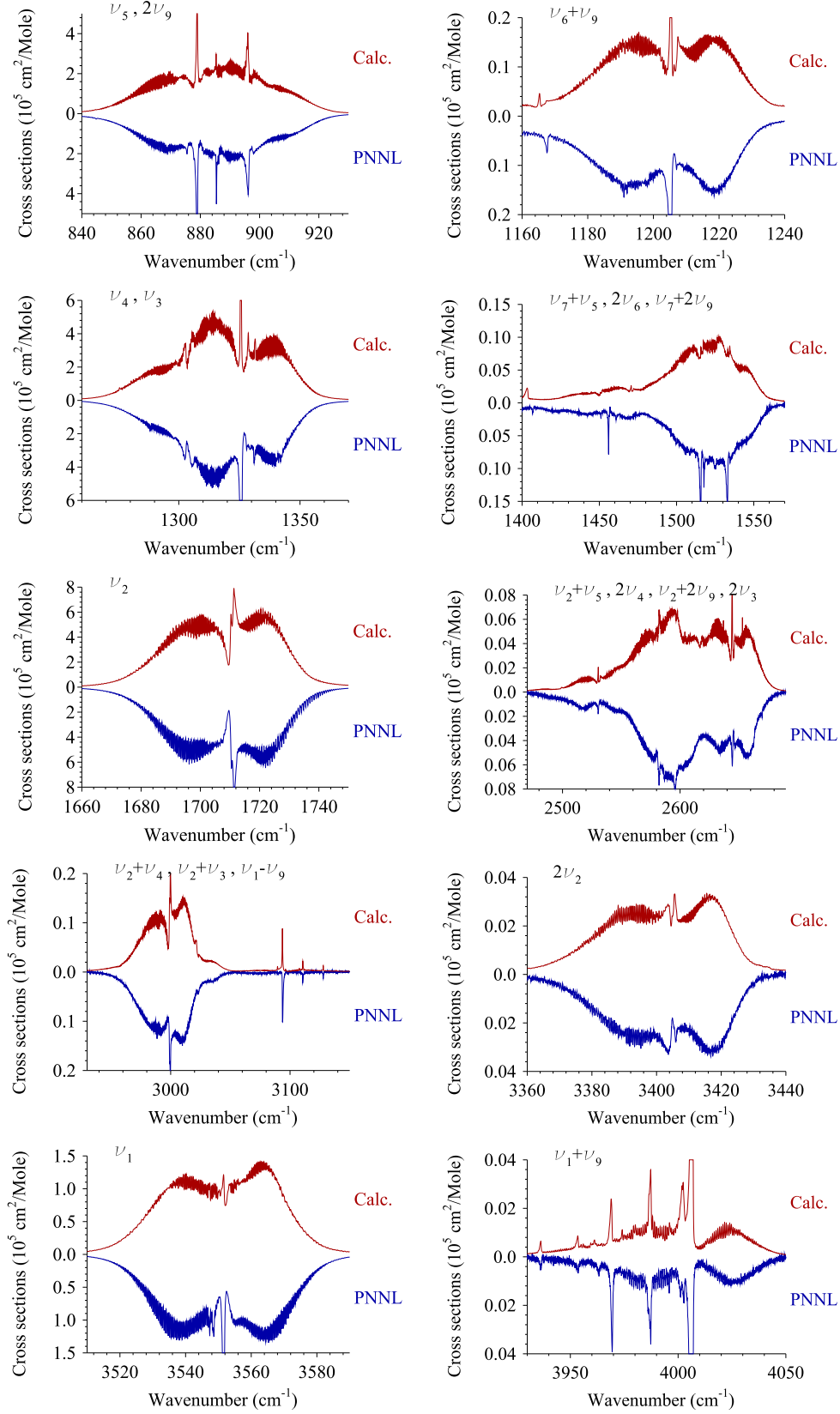


FIG. 7: Calculated (red curve) and experimental PNNL (blue curve) spectra in the region of the fundamental, first overtone and lowest combination bands.

and other studies on hot astronomical bodies, we are currently preparing an  $\text{HNO}_3$  line list which should be valid over an extended temperature range. This line list will be published elsewhere [86].

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